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Swelling Characterizations of the Interpenetrating Polymer Network Hydrogels Composed of Polymethacrylic Acid and Alginate

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A temperature- and pH-responsive interpenetrating polymer network (IPN) hydrogels constructed with polymethacrylic acid (PMAAc) and sodium alginate (SA) by sequential IPN method was studied. The characterizations of IPN hydrogels were investigated by fourier transform infra-red spectroscopy (FT-IR), differential scanning calorimetry (DSC) and swelling tests under various conditions.

IPN hydrogels exhibited a relatively high swelling ratio in the range of 183-916% at 25°C. The swelling ratio of PMAAc/SA IPN hydrogels depended on pH, temperature and ionic concentration. DSC was used for the quantitative determination of the amounts of freezing and non-freezing water. The amount of free water increased with increasing PMAAc content in the IPN hydrogels.

Keywords interpenetrating polymer network, swelling behavior, methacrylic acid, alginate

Introduction

An interpenetrating polymer network (IPN) is defined as a combination of two polymers which have the following two characteristics: firstly, one of the polymers must be synthesized or crosslinked in the immediate presence of the other, and secondly the combination provides the possibility of effectively producing advanced multi-component polymeric systems with new property profiles (1–4). Recently, IPNs have gained widespread acceptance in industrial applications and newer IPNs showing the possibility of a wider range of applications are emerging daily (5). Studies of hydrogels are interesting not only from a chemical point of view, but they are also being used in chemical engineering, pharmaceuticals, food processing, biochemistry, biology and medicine.

Sodium alginate (SA) is an abundant polysaccharide derived from sea algae. It is composed of a linear block copolymer of 1–4 linked β (beta)-D-Mannuronic acid (M) and α (alpha)-L-guluronic acid (G). Divalent ions form crosslinks in alginate by binding

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the guluronic residues, including a sol-gel transition in the material. An aqueous solution of alginate is readily transformed into a hydrogel on addition of metallic divalent cations such as Ca^{2+}. Due to its remarkable gelation properties, it has been widely used in food, fabric, and medicine. One of the useful characteristics of alginate is its ability to form hydrogels (6–8).

The industrial importance and the wide use of polyelectrolytes such as polyacrylic acid and polymethacrylic acid (PMAAc) is well known. PMMAc is known to be a model hydrophilic system and the crosslinked polymer of PMAAc has proved to be very useful in many biomedical applications (9).

Many researchers have reported the swelling behavior of polymers. Peniche et al. (10) reported the water sorption of flexible networks based on 2-hydroxyethyl methacrylate-triethylenglycol dimethacrylate copolymers. Shin et al. (11) reported on novel pH- and temperature-responsive IPN hydrogels composed of PVA and poly(acrylic acid) crosslinked by ultraviolet (UV) irradiation. Gan et al. (12) reported on water sorption studies of new pH-responsive N-acryloyl-N′-methyl piperazine and methyl methacrylate hydrogels.

In this paper, we report on the preparation and swelling properties under various conditions of PMAAc/SA IPN hydrogels. In addition, DSC studies were performed to observe the state of water for swollen IPN hydrogels.

Experimental

Materials

Sodium alginate (mannuronate/gluronate ratio of alginate (M/G) = 1.56), N,N′-methylenebisacrylamide (MBAAm) and MAAc monomer were purchased from Aldrich Chem. Co., USA. Ammonium peroxydisulfate (APS) and N,N,N′,N′-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chem. Co., Japan. Calcium chloride was purchased from Duksan Pure Chem. Co., Korea. All other chemicals were reagent grade and used without further purification.

Preparation of IPN Hydrogels

The IPN hydrogel was prepared using the sequential IPN method. SA was dissolved in deionized water for 6 h to make a 5 wt% aqueous solution. Next, the MAAc monomers were mixed in the desired proportions. The detail composition and designation of PMAAc/SA IPN hydrogels are listed in Table 1. MAAc was crosslinked in the presence of SA, using APS, TMEDA and MBAAm as initiator, accelerator and

Table 1
Composition and designation of PMAAc/SA IPN hydrogels

Sample	Feed Composition MAAc:SA (wt%)
MASA31	3:1
MASA11	1:1
MASA13	1:3

crosslinking agent, respectively. The contents of the initiator and the accelerator were 1 wt% of the monomer and the contents of the crosslinking agent were 3 mol% of the monomer. The optimum amount of solution was poured into a glass petri dish and cast in film formed by solvent evaporation at room temperature. After being dried, the film was removed from the glass petri dish and all were immersed in 1 wt% calcium chloride aqueous solution for 1 h. The prepared films were washed with deionized water to remove the unreacted calcium chloride.

Preparation of Hank's Solution

For the application of biosensors, *in vivo* tests are complicated, so swelling behavior is studied in simulated body fluids. Hank's solution is used to simulate the swelling behavior of PMAAc/SA IPN hydrogel in the human body fluid system. The composition of Hank's solution used in this paper is listed in Table 2.

Measurement

The swelling ratio of IPN hydrogels were measured in deionized water. Preweighed dry IPN films were immersed in solutions with various temperature, pH, and ionic concentration until they swelled to equilibrium. It was confirmed that 12 h equilibration was enough for the films to reach the equilibrium swelling. The swelling ratio can be calculated as a function of time.

$$\text{Swelling ratio } (\%) = \frac{W_s - W_d}{W_d} \times 100 \tag{1}$$

where, W_s is the weight of the swollen state at a given time, and W_d is the weight in the dry state. The equilibrium water content (EWC) using calculation for the state of water was calculated from the following equation (13):

$$\text{EWC } (\%) = \frac{W_e - W_d}{W_e} \times 100 \tag{2}$$

Table 2
Composition of Hank's solution

Composition	Concentration (g/l)
NaCl	8.00
Glucose	1.00
KCl	0.40
$NaHCO_3$	0.35
$CaCl_2$	0.14
$MgCl_2 \cdot 6H_2O$	0.10
$Na_2HPO_4 \cdot 2H_2O$	0.06
KH_2PO_4	0.06
$MgSO_4 \cdot 7H_2O$	0.06

where, W_e represents the weight of the swollen state at equilibrium. The swelling experiments were repeated 3 times until there was no further weight increase.

The state of the water in the IPN hydrogels was investigated by DSC (Du Pont Instruments DSC 910). The IPN hydrogels equilibrated in deionized water were cooled to $-20^{\circ}C$ and then rescanned up to $20^{\circ}C$ at a heating rate of $5^{\circ}C/min$ under N_2 flow. The amount of free water and bound water was calculated from the melting enthalpies (14, 15).

Results and Discussion

FT-IR Spectroscopy

FT-IR spectroscopy (Nicolet Model Magma IR 550) was used to confirm the structure of SA/PDADMAC IPN hydrogels. In SA's FT-IR spectrum at $1605\,cm^{-1}$ stretching due to $-COO^-$ asymmetric stretching, $1420\,cm^{-1}$ due to $-COO^-$ symmetric stretching and $1030\,cm^{-1}$ due to $-O$ stretching can be confirmed. In PMAAc's FT-IR spectrum there is C═O stretching vibration of carboxylic groups at $1694\,cm^{-1}$ and $1050\,cm^{-1}$ due to $-CH_3$ groups can be confirmed. In the FT-IR spectrum of PMAAc/SA IPN, the absorption peaks belonging to two components can be confirmed, such as at $1605\,cm^{-1}$ due to $-COO^-$ asymmetric stretching, $1420\,cm^{-1}$ due to $-COO^-$ symmetric stretching of SA and C═O stretching in the carboxylic groups at $1694\,cm^{-1}$ and $1050\,cm^{-1}$ due to $-CH_3$ groups of PMAAc.

Swelling Behavior

The swelling ratio of IPN hydrogels was calculated according to Equation (1) and the swelling kinetics of IPN hydrogels in deionized water at room temperature are plotted in Figure 1. All hydrogels swelled rapidly and reached equilibrium within 2 h. The swelling ratio of IPN hydrogels increased to 183–916% as increased with PMAAc

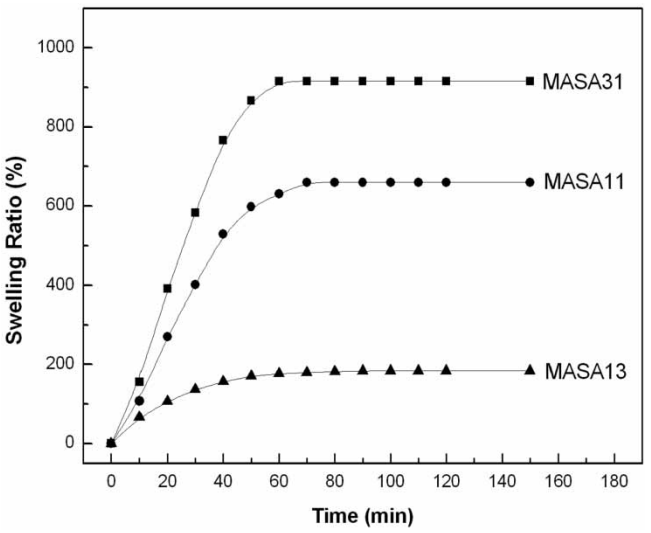

Figure 1. Swelling kinetics of IPN hydrogels.

content. Because PMAAc is more hydrophilic than alginate, the MASA31 sample that contained the highest amount of PMAAc among sample showed the highest swelling ratio.

Figure 2 shows the temperature-sensitive swelling behavior of MASA31 in deionized water at 25, 35 and 45°C. A water molecule will gain an enthalpy during an increase in temperature, and the hydrophilic group in the PMAAc/SA IPN hydrogel will be turned into an intramolecular hydrogen bond in this condition (16). We can expect that MASA31 at 25°C has a more compact complex structure than at other temperatures. As the temperature of the PMAAc/SA IPN hydrogels in swelling states increases, the swelling ratio grew higher. The PMAAc/SA IPN hydrogel exhibited temperature-dependent swelling behavior due to the association/dissociation of hydrogen bonding by carboxyl groups in PMAAc and SA within IPN hydrogels (17).

State of Water

Generally, the state of water in the polymer can be classified as free water, freezing bound water and non-freezing bound water. Free water is water, which does not take part in hydrogen bonding with polymer molecules. It has a similar transition temperature, enthalpy and DSC curves as pure water. Freezing bound water, intermediate water is water, which interacts weakly with polymer molecules. Non-freezing water, also known as bound water is water molecules which are bound to polymer molecules through hydrogen bonds. Non-freezing of water shows no endothermic peak in the temperature range −70 to 0°C. Figure 3 shows the DSC thermograms of a water swollen PMAAc/SA IPN sample. Two melting peaks can be seen in the DSC curves in the IPN hydrogels, indicating that free water and freezing bound water exist in the IPN hydrogels.

The amount of free water and bound water was calculated from the melting enthalpies. The following equation assumes that the heat of fusion of the free water in the hydrogel was the same as that of the ice (18):

$$W_b\ (\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{endo}/Q_f) \times 100$$

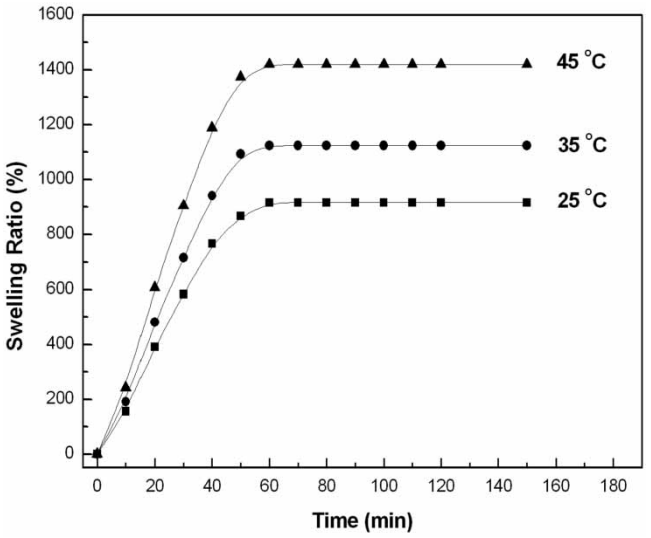

Figure 2. Swelling behavior of IPN hydrogel as a function of temperature.

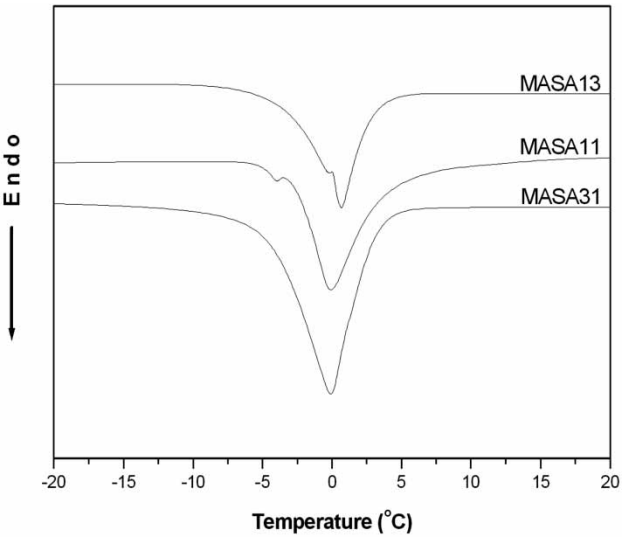

Figure 3. DSC thermograms of swollen IPN hydrogels.

where W_t is the EWC (%) as shown in Equation (2); W_b, the amount of bound water (%); W_f and, W_{fb}, the amount of free water and freezing bound water, respectively. Q_{endo} and Q_f are the heat of fusion of the free water in the IPN hydrogel and that of the ice (79.9 cal/g), respectively.

Figure 3 illustrates the free water melting thermograms of IPN hydrogels. As a rule, DSC is used to determine the amount of free water that is not bound by hydrogen bonding. The fraction of free water in the total water is approximately calculated as the ratio of the endothermic peak area for water swollen hydrogel to the melting endothermic heat of fusion for pure water. Figure 4 shows the content of water corresponding to free and bound water as well as total water. The amount of free water increased with increasing

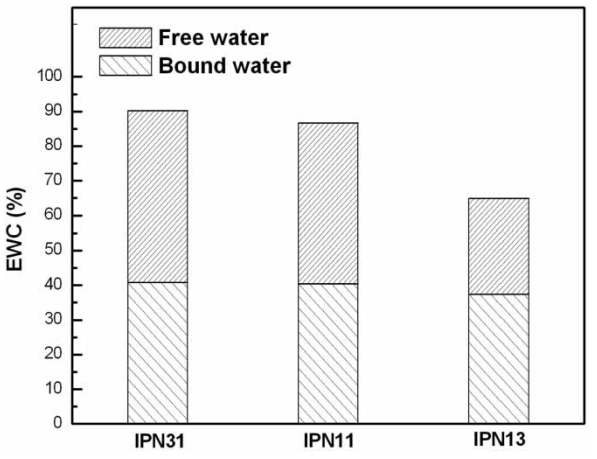

Figure 4. Content of water corresponding to free, bound and total water in IPN hydrogels.

PMAAc content in the IPN hydrogels. This indicates that the increase of the swelling ratio is attributed mainly to the free water content in the PMAAc/SA IPN hydrogels.

Effect of pH

For characterization of the response of PMAAc/SA IPN hydrogel to the change in the external pH condition, IPN hydrogel was allowed to swell to equilibrium in an aqueous swelling medium of pH 2 to 6 at 25°C. The effects of the external pH on the swelling behavior of IPN hydrogel is summarized in Figure 5. In this experiment, we chose the MASA31 which swelled higher than the others as shown in Figure 1.

When carboxylic acid groups are below pK_a of alginate (about 3.2 and 4 for guluonic and mannuronic acids, respectively), they are in the form of COOH. As the pH of the solution increases, COOH becomes ionized to COO^-, and the resulting electrostatic repulsion causes the hydrogels to swell. In the case of PMAAc/SA IPN hydrogels, carboxylic acid coexists in alginate and PMAAc. Also, above pK_a of carboxylic acid in PMAAc (about 5.5), the carboxylic acid groups become ionized to COO^-, and the IPN hydrogel swelled to a large volume change due to the development of a large osmotic swelling force caused by the presence of the ions. As shown in Figure 5, the equilibrium swelling ratio of PMAAc/SA IPN hydrogel increased with increased pH values.

Effect of Ionic Concentration

The effect of the concentration of the HCl aqueous solution on the equilibrium swelling was studied for the PMAAc/SA IPN hydrogel. Figure 6 shows the equilibrium swelling ratio of the PMAAc/SA IPN hydrogel in aqueous HCl solutions at room temperature. It shows that the swelling ratio decreased with an increase in the concentration of the HCl solution. Generally, the swelling ratio of PMAAc/SA IPN hydrogel depends on the association state of the ionic group within the polymer and on the affinity of the

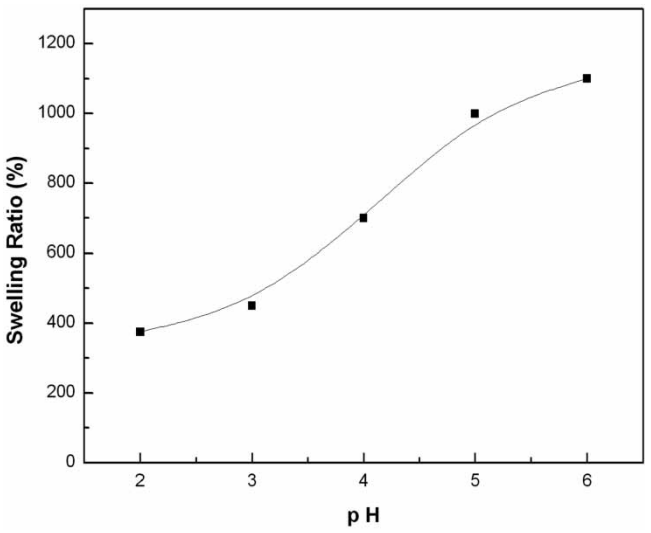

Figure 5. Swelling behavior of IPN hydrogel as a function of pH.

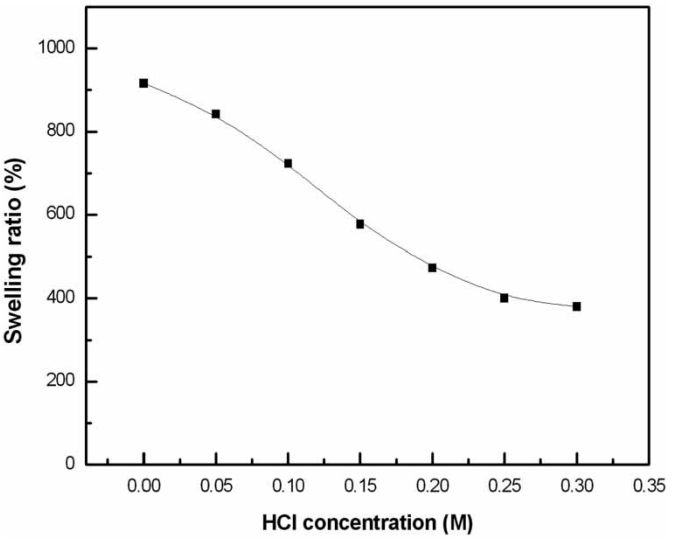

Figure 6. Swelling behavior of IPN hydrogel as a function of ionic strength.

complex for water. According to the Donnan osmotic pressure equilibrium, an increase of movable counterions in the solution leads to a decrease of osmotic pressure within the gel and causes shrinkage of the gel (19).

Swelling Behavior in Hank's Solution

For biomedical applications, the swelling kinetic of PMAAc/SA IPN hydrogel in Hank's solution is shown in Figure 7. As shown in Figure 1, the swelling ratio of MASA31

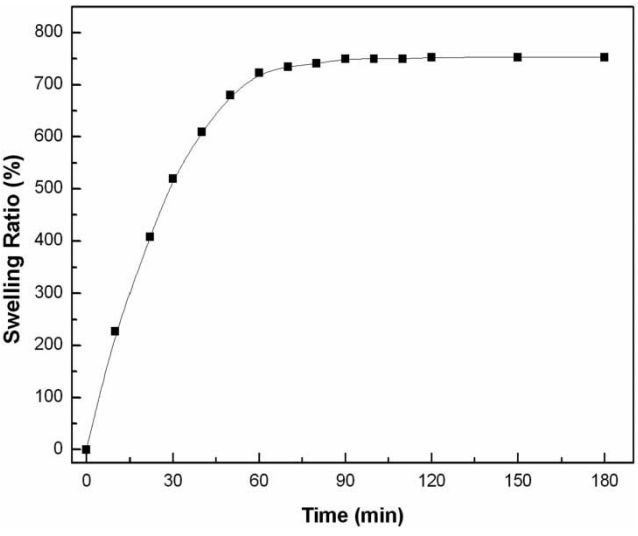

Figure 7. Swelling kinetics of the IPN hydrogel in Hank's solution.

exhibited 916% in deionized water. However the swelling ratio of MASA31 exhibited 762% in Hank's solution. The result of the swelling ratio in Hank's solution is lower than in deionized water because of the shielding effect of ions shown in Table 2.

Conclusions

IPN hydrogels were prepared based on PMAAc and SA by the sequential IPN method. The swelling behaviors at various temperature, pH and ionic concentrations were investigated. The PMAAc/SA IPN hydrogels exhibited a relatively high swelling ratio as PMAAc content increased. The MASA31 sample that contained the highest amount of PMAAc among the samples showed the highest swelling ratio. Also, the amount of free water increased with increasing PMAAc content in the IPN hydrogels.

The PMAAc/SA IPN hydrogels exhibited a swelling change in response to external stimuli such as temperature, pH and ionic concentration, and could be useful as novel modulation systems in the biomedical field.

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